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Introduction.

In these report we continue to describe the results obtained in the course of the investigation of the electrochemical properties of gel-type polymer electrolytes formed by immobilization of liquid solutions (e.g., solutions of lithium salts in propylene carbonate-ethylene carbonate, PC/EC , mixtures) in polymer (e.g., poly(acrylonitrile), PAN) matrices. In particular, we have continued to investigate the characteristics and the properties of the interface with the lithium metal electrode, in order to complete task (i) which is focused on the carification and the understanding of the basic properties of the gel-type, polymer electrolytes (see previous reports).

Task (i)- Clarification of the lithium interface phenomena

Experimental.

The preparation of the PAN-based gel electrolytes has been described in previous reports(1). Three representative examples of PAN-based gel electrolytes have been considered, namely the systems having the following molar composition :

PAN:16/PC:23/EC:56.5/LiX: 4.5

where the LiX salt used was $LiClO_4$, $LiAsF_6$ and $LiN(CF_3SO_2)_2$ (high purity, reagent grade compounds), respectively. This composition gives a solvent (PC:EC mixture) to salt (LiX) molar ratio of 17.6 to 1, a value which was found to be the most suitable for assuring complete miscibility of the various components and, ultimately, a full homogeneity of the final electrolytic membranes. For simplicity reasons, the three types of electrolytes considered in this work will be hereafter indicated as:

a) $LiClO_4$ - PC/EC-PAN
b) $LiN(CF_3SO_2)_2$ -PC/EC-PAN
c) $LiAsF_6$ -PC/EC-PAN

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For comparison reasons, we have also considered electrolytes formed by immobilizing into a PAN matrix solutions of lithium salts in γ-butyrloctone, BL. For simplicity, these electrolytes will be hereafter indicated as:

d) $LiClO_4$ - BL- PANb)
e) $LiAsF_6$ -BL-PAN

Results.

Previous data (1,2) suggested that lithium electrodes may undergo passivation when in contact with PAN-based gel electrolytes. To further investigate this crucial aspect we have continued to analyze the phenomena occuring at the interface by carrying out a detailed impedance study of symmetrical cells of the Li/electrolyte/Li type, stored under different conditions. The methodology has been described in details in the previous report (2).

The results, which wereinterpreted on the basis of a suitable equivalent circuit (2), indicated that the Li interfacial resistance increases upon time of storage with a trend which suggested that the passivation of lithium in the PAN-based electrolytes may be severe to the point of inducing the growth at the interface of a layer having a resistance orders of magnitude higher than the bulk resistance of the electrolyte itself. On the other hand, the observed passivation phenomena are not unexpected since, as discussed in previous reports (1), some of the electrolyte components, i.e. EC and, particularly PC, which are very aggressive lithium corroding agents, spontaneously evaporate off the bulk to continuously reach the interface and attack the metal.

This would pose some major questions on the effective applicability of these gel electrolytes. On the other hand, the kinetics of passivation sems to vary passing from one electrolyte to another (2) this leading to the reasonable conclusion that the nature of the liquid solution trapped in the gel matrix may have an influence on the corrosion mechanism. Therefore, one may hope that the selection of a proper solvent-salt combination may limit the extent of the passivation. We have attempted to control this aspect, by examining gel electrolytes forming by trapping solutions of lithium salts in γ-butyrolactone, BL (namely a solvent much less aggressive than PC or EC) into a PAN matrix.

The stability of the lithium interface, again evaluated in terms of changes in interface resistance determined by following the time evolution of the impedance of symmetrical Li/ PAN-BL-

LiX/Li cell, is illustrated by Figure 1. One may notice that, while passivation of lithium is also experienced in PAN-BL media, substantial improvement is obtained in terms of growth kinetics and thickness of the resistive layer, especially in the case of the PAN-BL-LiAsF6 electrolyte, this confirming that the nature of the electrolyte components may indeed play a key role in controlling the stability of the lithium interface.
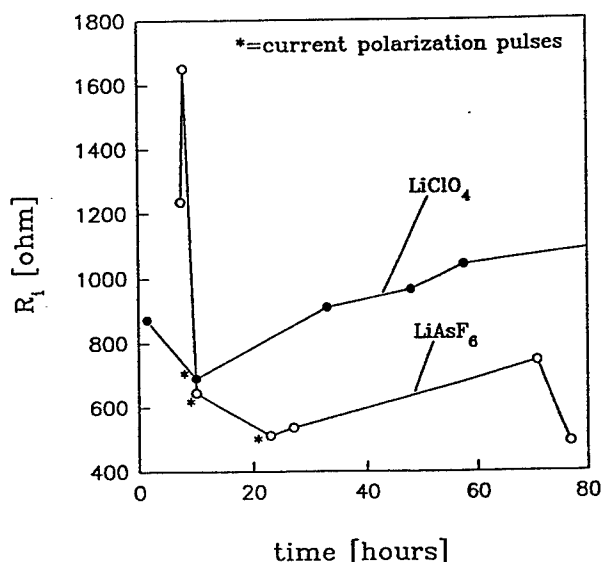

Figure 1 -Time evolution of the interfacial resistance , R$_i$,of the lithium electrode in contact with the LiClO$_4$ BL- PAN, curve a , and the LiAsF$_6$ BL -PAN, curve b electrolytes.

However, to rationalize this effect and thus, to finally identify the most promising approaches for controlling the lithium passivation, it is essential to reach a more precise idea of the nature and the morphology of the film growing on the lithium surface. Figure 2 illustrates the evolution of the resistance and of the capacitance of the passivation film growing on the lithium electrode in contact with a PAN EC/PC LiClO$_4$ electrolyte. The capacity values, again determined by interpreting the impedance data with an equivalent circuit analysis (2), initiallly decrease, to then rise and finally decay. Remembering that the capacity C is directly related to the surface area A and to the thickness of the film by the well known equation:

$$C = \frac{\varepsilon \varepsilon_o A}{d} \qquad [1]$$

where ε and ε_0 are the dielectric constants of the film and the vacuum, respectively, one can explain the C and Ri trends of Figure 2 by assuming that the interfacial structure may be represented by the multilayer model illustrated in Figure 3.
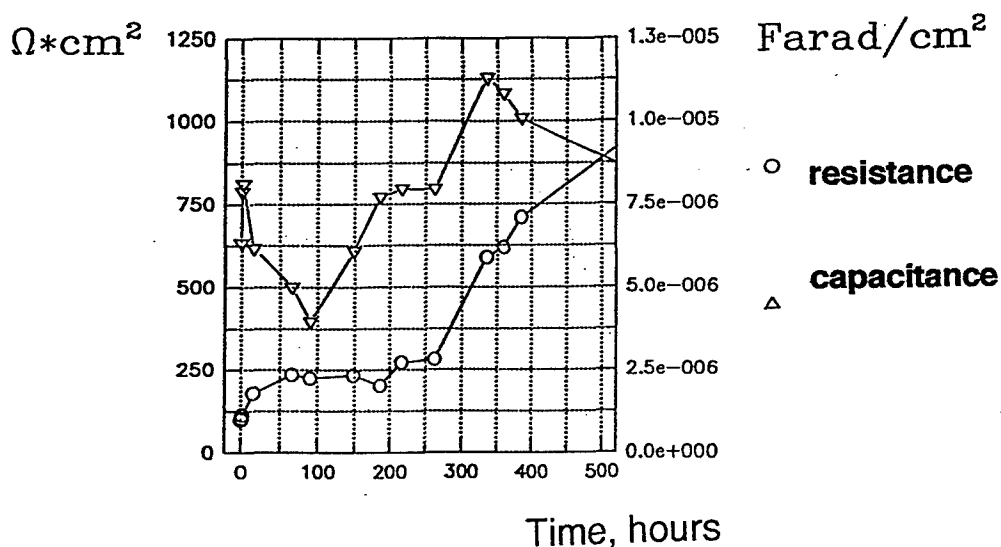

Figure 2.Evolution of the resistance and of the capacitance of the passivation film growing on the lithium electrode in contact with a PAN EC/PC LiClO$_4$ electrolyte.

According to this model, lithium experiences upon initial contact with the electrolyte a first passivation reaction with the formation of a compact layer which grows directly on the metal surface (or on a native film). Accordingly, the interfacial capacitance decreases and the resistance increases. On prolonged contact time, the passivation phenomena give rise to an additional, porous layer, whose nature and morphology probably depend upon the type of solvent, the type and amount of impurities and upon other unpredictable causes. Until this additional layer remains porous, its surface area is large, hence the capacitance decreases while the resistance increases. With proceeding contact times, the layer becomes progressively denser, to finally collaps on the electrode interface, with the consequent decay in capacitance and sharp rise in resistance. Therefore, the model of Figure 3 suggested that is the second, thick layer the one which mostly affects the lithium electrode performance and

hence, that care should be directed to inhibit its formation and growth.

1) native ed initial compact layer.
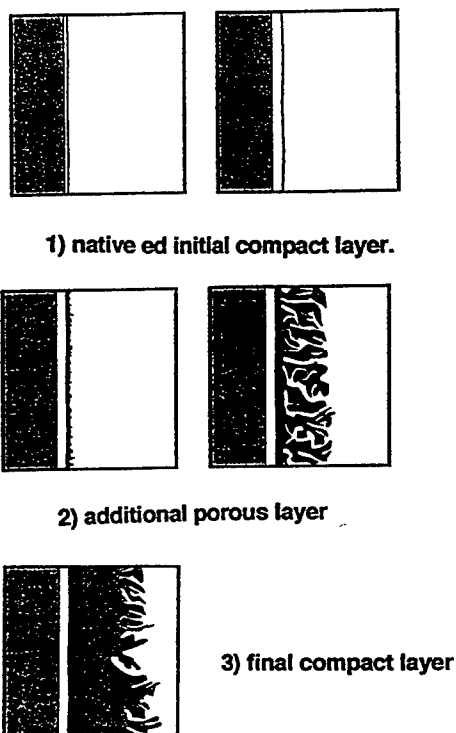
2) additional porous layer

3) final compact layer

Figure 3 - Multilayer model of the Lithium/ PAN-based electrolyte interfacial structure.

One approach in this direction is the already cited selection of solvents which are expected to be the less aggressive towards the lithium metal. A second one is the addition to the electrolyte of materials which may act as impurity-getters, namely of substances capable of trapping the impurities so preventing their flow to the interface. Ceramic fillers, like γ-lithium alluminate or zeolyes, are expected (3) to satisfactorily fulfill this action.These expectation are confirmed by practical results, in fact, addition of zeolytes to the PAN EC/PC LiClO4 electrolyte considerably alleviates the passivation of the lithium electrode, as shown by Figure 4 which compares the trend of the interfacial resistance of a Li electrode in cantact with plain and with zeolyte-added electrolytes.
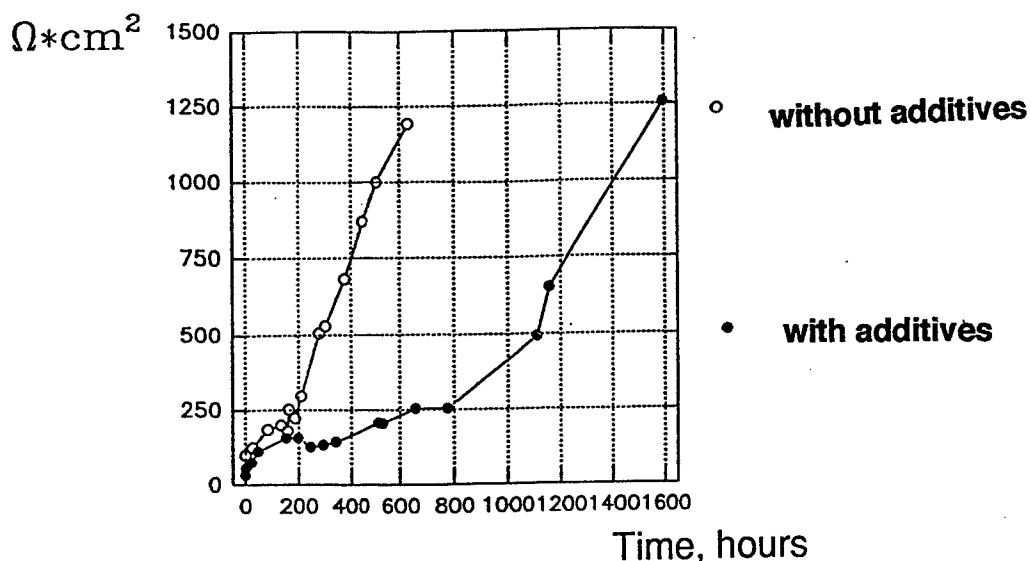
$\Omega*cm^2$

Time, hours

Figure 4 -Time evolution of the interfacial resistance, Ri, of the lithium electrode in plain (--o--) and in zeolite-added (--●--) PAN-EC/PC LiClO$_4$ electrolyte. (Room temperature).

The beneficial effect of the ceramic fillers on the conditions of the lithium interface is further confirmed by the comparison of cycling efficiency obtained in plain and in composite gel electrolytes. The evaluation was carried out by first plating an excess of lithium on a stainless-steel substrate and then galvanostatically cycling a fraction of the total charge until full lithium consumption was experienced. The cycling efficiency E was then determined by the relation:

$$E = \frac{Q_s - Q_{ex}/n}{Q_s} \qquad [2]$$

where Q_s = charge cycled, Q_{ex} = charge of excess plated lithium and n= number of cycles.

The results gave cycling efficiency values which passed from E =72% in the case of a cell using a plain PAN, EC/PC LiClO$_4$ electrolyte to a value E=85% for a cell using a composite PAN EC/PC LiClO$_4$+10 weight percent zeolytes electrolyte. Although encouraging this improvement is still insufficient for practical purposes. In fact, for assuring acceptable applicability, i.e. the efficiency should fall between 97 and 99% . Therefore, further study will be devoted to this problem with the aim of improving the knowledge of the interfacial phenomena and of

identifying the effective route for assuring sufficiently high ciclability.

References.

1- Contract SPC-92-4003, Final Report.
2- Contract SPC-93-4003, First two-month Progress Report.
3- F.Croce and B.Scrosati, *J.Power Sources,* 44 (1993) 9.